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Synergistic effect of Ni and Fe in Fe-doped NiS_2 counter electrode for dye-sensitized solar cells: Experimental and DFT studies

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ABSTRACT

Uniform Fe-doped NiS_2 octahedrons with the size of ~250 nm have been prepared by a hydrothermal method. The as-synthesized Fe-doped NiS_2 octahedrons exhibit excellent electro-catalytic activity for the reduction of triiodide to iodide in dye-sensitized solar cells (DSCs). The DSC with Fe-doped NiS_2 octahedrons CE demonstrates a power conversion efficiency (PCE) of 8.01%, higher than those of NiS_2 CE (6.90%) and FeS_2 CE (4.13%). The enhanced efficiency is attributed to the synergistic effect between Ni and Fe ions in Fe-doped NiS_2 octahedrons. Density functional theory (DFT) calculations reveal the adsorption energy of I (*E*I ad) increases from −0.14 eV (NiS_2) to −0.65 eV (Fe-doped NiS_2) after Fe doping, leading to an enhanced solar cell performance. This study indicates that the Fe-doped NiS_2 octahedron is a promising substitute to develop non-Pt CEs in DSCs.

1. Introduction

More efforts have been dedicated to explore clean, renewable and sustainable energy sources to satisfy the increasing energy demands and reduce environmental problems [1–4]. Dye-sensitized solar cells (DSCs) converting solar energy to electrical energy have attracted considerable attention due to its high power conversion efficiency (PCE), low cost, and environmentally benign [5–9]. Typical DSC consists of counter electrode (CE), photoanode adsorbed by dye molecules and electrolyte containing triiodide/iodide (I_3^-/I^-) redox couple. Pt is the most widely CE due to its high efficient catalysis towards the reduction of I_3^- to I^-. However, the low abundance and high cost of Pt strongly hinders the commercial application in DSCs [10]. To overcome these drawbacks, more efforts have been made to hunt for low cost, earth-abundant and highly efficient materials, including transition metal carbides [11], oxides [12,13], and nitrides [14].

Among various transition metal compounds, metal sulfide electrodes [15,16], such as Co_9S_8 [17], CoS_2 [18], SnS_2 [19] and MoS_2 [8], have been investigated to replace Pt CEs because of their good electro-catalytic activity, high conductivity, non-toxicity and high abundance. Nickel sulfides have excellent electrocatalytic activity and conductivity. In our previous work, DSC based on NiS_2 octahedron enclosed by {111} planes delivered a PCE of 5.98% [20]. Li et al. fabricated NiS_2 hollow spheres CE giving a PCE of 7.13% [21]. However, the PCE of DSCs based on NiS_2 CEs is still uncompetitive, it is necessary to modify the NiS_2 as an efficient CE in DSCs. Among various modification methods to improve the PCE, introducing new elements into original phases seems to be an effective strategy [3,22]. For instance, Su et al. reported a $Co_{1/2}Mo_{1/2}S_2$ ternary nanosheets with a PCE of 9.16%, superior to those of binary MoS_2 (8.27%) and CoS_2 (7.18%) [23]. The electro-catalytic activity of MoS_2 towards reduction of I_3^- to I^- ions is improved by introducing Co. Therefore, by introducing a new element into NiS_2 octahedron, the DSCs performance is expected to be further improved.

Herein, we report a facile hydrothermal approach to prepare Fe-doped NiS_2 octahedrons. The as-obtained uniform Fe-doped NiS_2 octahedrons with the size of ~250 nm are introduced to DSCs as a CE material without any post-treatment. The fabricated device

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yields a high PCE of 8.01% under 100 mW cm^{-2}, superior to those DSCs based on NiS_2 octahedrons (6.90%) and FeS_2 CE (4.13%). The synergistic effect of Ni and Fe ions in Fe-doped NiS_2 octahedrons can effectively improve the catalytic activity. Density functional theory (DFT) was used to disclose the synergistic effect by calculating the adsorption energy of I (*E*I ad). These results demonstrate the Fe-doped NiS_2 octahedrons are attractive CE materials for high-efficiency DSCs, and thus provides a very promising approach for the commercialization of Pt-free large-scale DSCs.

2. Experimental

2.1. Preparation of Fe-doped NiS_2 and FeS_2 octahedrons

In the synthesis of Fe-doped NiS_2 octahedrons, 0.1 mmol of $NiCl_2 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ (molar ratio of 19/1), 0.25 mmol of $Na_2S_2O_3 \cdot 5H_2O$ and 0.055 g of polyvinylpyrrolidone (PVP, MW 58 000) were dispersed in 40 mL ultrapure water in a Teflon-lined autoclave (50 mL), which was maintained at 150 °C for 12 h. Finally, a centrifugation procedure was used to collect the product. FeS_2 octahedrons were synthesized by dispersing $FeCl_2 \cdot 4H_2O$ (1 mmol), S powder (0.2 g), PVP (0.525 g), and NaOH aqueous solution (4 mmol, 5 mL) in 38 mL ethylene glycol in a Teflon-lined autoclave (50 mL), which was maintained at 180 °C for 12 h. NiS_2 octahedrons were prepared according to the reported method [20].

2.2. Characterizations

The structure and morphologies of the samples were characterized by X-ray diffraction (XRD, Rigaku Dmax 2200 X-ray diffraction), transmission electron microscopy (TEM, JEOL JEM-2100F) and scanning electron microscope (SEM, Hitachi 7500), respectively. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 photoelectron spectrometer with an Al Kα X-ray source and a power of 150 W. The element content was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Prodigy 7 system). Cyclic voltammetry (CV), Tafel polarization and electrochemical impedance spectroscopy (EIS) were performed on a CHI660E electrochemical workstation (Shanghai Chenhua Co. Ltd., China) using a three-electrode system. These measurements were carried out in an acetonitrile solution (10.0 mM NaI, 1.0 mM I_2, and 0.1 M $NaClO_4$). In the experiments, a Pt foil and an Ag/AgCl electrode were used as the counter and reference electrode, while Pt, Fe-doped NiS_2 octahedrons, NiS_2 octahedrons, and FeS_2 octahedrons were separately used as the working electrode. The photocurrent density-photovoltage (J-V) curves were measured by an Oriel solar simulator 91160 (AM 1.5 G, 100 mW cm^{-2}) with the electrochemical workstation.

2.3. Cell fabrication

Pt CE was prepared by dropping 130 μL of H_2PtCl_6 in isopropanol (5 mM) on a 0.25 cm^2 FTO glass (14 Ω square^{-1}) followed by heat treatment at 400 °C for 30 min. 12.5 mg of Fe-doped NiS_2, NiS_2 and FeS_2 octahedrons were dispersed in 1 mL of ethanol, respectively. 10 μL of the solutions were dropped on the FTO glass with 0.25 cm^2. The materials loading amounts was 500 μg cm^{-2}. The photoanodes were prepared according to our reported work [20]. The acetonitrile electrolyte (0.03 M I_2, 0.06 M NaI, 0.1 M guanidinium thiocyanate, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide and 0.5 M 4-*tert*-butylpyridine) was injected into the interspace between photoanode and Pt CE. Other DSCs were assembled using Fe-doped NiS_2 octahedrons, NiS_2 octahedrons and FeS_2 octahedrons CEs instead of Pt CE.

2.4. Calculation method

Calculations were based on DFT in conjunction with projector augmented wave (PAW) potentials, as implemented in the Vienna *ab initio* simulation package (VASP) [24]. The generalized gradient approximations (GGA) [25] of Perdew-Burke-Ernzerhof (PBE) [26] were chosen together with Hubbard-U term fixed at 5.5 (3.3) eV for Ni (Fe) from linear response theory [27]. We took the effect of solvent implicitly into account by introducing CH_3CN solvent molecules with density of 0.79 g/cm^3 above the (111) slab models. The *E*I ad was defined as [28]:

$$E_{ad}^{I} = E(I/\text{interface}) - E(\text{interface}) - 1/2(I_2)$$

where E(I/interface), E(interface), and E(I_2) were the energies of I adsorbed on the liquid/electrode interface, the liquid/electrode interface, and I_2 in the gas phase, respectively.

3. Results and discussion

To characterize the crystallinity and structure of the as-prepared samples, XRD was carried out. As shown in the XRD patterns of Fig. 1, the main peak positions of Fe-doped NiS_2 were identical to those of NiS_2 (JCPDS No. 11-0099), confirming that the sample was pure phase with high crystallinity. Obviously, the incorporation of Fe did not affect the crystal structure and there was no new peak originating from iron sulfides, possibly due to the homogeneous incorporation of Fe ions into the lattice of NiS_2 by taking the sites of Ni ions [22,29]. NiS_2 and FeS_2 nanoparticles were also prepared and characterized by XRD. The patterns could be indexed to the standard NiS_2 (JCPDS No. 11-0099) and FeS_2 (JCPDS No. 42-1340), respectively. Compared with pure NiS_2, the XRD patterns of Fe-doped NiS_2 revealed a small peak shift to high angle, indicating the successful doping of Fe ions into the lattice of NiS_2.

To characterize the elemental composition and the metal electronic states of the as-prepared samples, X-ray photoelectron spectroscopy (XPS) was performed. As shown in Fig. S1, the peaks of Ni, Fe, and S came from the Fe-doped NiS_2. The high-resolution spectrum of Ni 2p (Fig. S1a) demonstrated that the binding energies (BEs) of 853.7 and 856.1 eV in the Ni 2p region of the spectra came from the Ni-S and the surface oxidized Ni species, respectively, and the peak at 860.3 eV was indexed into the satellite of the Ni 2p peak [30]. As shown in Fig. S1b of Fe 2p region, the signal at

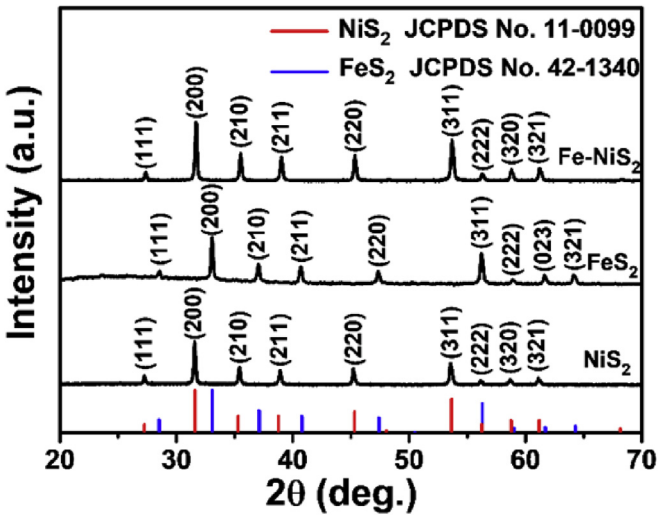

Fig. 1. (a) XRD patterns of Fe-doped NiS_2, FeS_2, and NiS_2 octahedrons.